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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

TWELFTH QUARTERLY TECHNICAL SUMMARY REPORT
1 July - 30 September 1964

Contract No. Nonr-3599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D. C.

DDC

NOV 1 , 1964

MIDWEST RESEARCH INSTITUTE
425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 4-0202

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by

Thomas A. Miln~
Frank T. Greene

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PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR. The report presents data on direct sampling of O, H, and OH radicals from one atmosphere flames, plus a summary of the quantitative sampling results achieved so far.

The research staff consists of Dr. Thomas A. Milne, project leader, and Dr. Frank T. Greene.

Approved:

MIDWEST RESEARCH INSTITUTE

Sheldon L. Levy, Director
Mathematics and Physics Division

12 November 1964

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SUMMARY

The free radical OH has been quantitatively sampled from H_2-O_2 and CH_4-O_2 one atmosphere flames at temperatures from 2300 - 3000°K. Oxygen atoms and hydrogen atoms have also been sampled from H_2-O_2 flames. A summary is given of equilibrium constants for various high temperature equilibria studied so far in this program. Agreement is within a factor of two in K_{eq}. in almost every case.

I. INTRODUCTION

Work has continued in the past quarter on the verification of the ability to quantitatively extract very reactive species from one atmosphere flames using a properly designed aerodynamic molecular beam sampling system. Described below are studies of O, H, and OH radicals in H_2-O_2 and CH_4-O_2 flames, a summary of quantitative third law checks on known equilibria in flames, and preparations and plans for studies of unknown and condensible species.

II. HYDROXYL RADICALS SAMPLED FROM H_2-O_2 AND CH_4-O_2 FLAMES

In attempting to quantitatively sample OH radicals in flames, a problem arose which was similar to that previously encountered with O atoms. It is necessary to distinguish 17^+ ions from neutral OH from 17^+ ions formed by fragmentation of H_2O, which is usually present in much larger quantity than OH. This problem is aggravated by a suspected but unknown temperature dependence of fragmentation of species like H_2O and O_2. If the room temperature cracking pattern of O_2 and H_2O is not too much altered at temperatures up to 3000°K, then fragmentation of O_2 and H_2O poses no problem at a nominal ionizing energy of 20 ev for the flames studied so far. In view of the rather large change in the cracking pattern of CO_2 with temperature, however, it would be desirable to check this unambiguously for O_2 and H_2O. The problem is much more difficult in this case, however, since we are simultaneously trying to show that the OH and O species can be quantitatively sampled.

A large number of flames, burned on a standard glass blowing torch, have been studied. In most cases, except for the hottest, fastest flames, gases were sampled at 1 mm. from the visible reaction zone. The $18^+/17^+$ ratios are shown for these flames in Table I at 20 and 50 ev, together with flame composition, theoretical flame temperature and theoretical ratio of H_2O/OH in the burnt gases. Two things are noticed. First, the $18^+/17^+$ ratios at 50 ev are scattered but virtually independent of temperature. Second, the 20 ev ratios correlate well with the theoretical H_2O/OH ratios as indicated in the last column. It seems clear that the 17^+ signal observed at 20 ev is mainly due to OH radical. The differences from the theoretical values may be due to differences in cross-section at 20 ev, departure of the flame from equilibrium temperature or composition, some contribution from fragmentation, as well as failure to quench. In general, it once again appears that we are sampling quantitatively to within our previous third law criterion of a factor of two in the equilibrium constant.

TABLE I

ION INTENSITY RATIOS, H_2O^+/OH^+, FOR A NUMBER OF H_2-O_2 AND CH_4-O_2 FLAMES AT 20 AND 50 EV IONIZING ELECTRON ENERGY

Flame Composition (Mole Ratios)					Adiabatic Flame Temp. (°K)	H_2O^+/OH^+		Calc. H_2O/OH	Obs/Calc
H_2	CH_4	O_2	N_2	Ar		50 ev	20 ev		
3		1			3004		21.3	10.1	2.1
2		1	1		2889		15.8	8.5	1.9
	1	4			2845	2.5	8.3	4.0	2.1
4		1			2830	2.9	35.8	24.9	1.4
2		3			2720	2.6	11.9	6.5	1.8
2		1	2		2709	3.1	19.7	14.2	1.4
5		1			2627	3.3	52.3	66.7	0.78
	1	1			2611	3.2	37.3	64.0	0.58
2		4			2570		11.4	8.3	1.4
2		1	3		2524	2.8	21.7	26.6	0.82
	1	2		8	2490	2.7	73.6	17.0	4.3
	1	2.4		8	2485	3.0	22.3	12.8	1.7
	1	1.8		8	2442	3.8	52.5	28.6	1.8
5		1	1		2360		53.7	267.	0.20
2		1	4		2334	3.0	32.5	56.0	0.58
2		5			2330	2.8	14.6	15.7	0.93
	1	8			2330	2.5	9.8	13.1	0.73
	1	1.6		8	2296	3.4	> 170.	117.	> 1.5

Several of these flames will be studied more completely on sheathed burners, with line reversal temperature measurements, to establish the detailed behavior to be expected for flames to be used in thermochemical studies.

One of the problems requiring further study is the relative cross-section dependence at low electron energy for, say, H_2O and OH. One may be boxed in between increasing fragmentation contributing to OH^+ at higher energies and the possibility of rapidly changing relative cross section for H_2O^+ and parent OH^+ ions at low energies. There is some indication of a plateau in the ratio of H_2O^+/OH^+ around 20 ev and in the following we simply assume equal cross sections at 20 ev and no fragmentation contribution.

Oxygen atoms have been observed in a number of the flames of Table I. H_2O appears to make a completely negligible contribution to O^+ at 20 ev and the contribution to O^+ from O_2 also appears negligible at 20 ev, based on the $CO-O_2$ flame work reported previously.[1] Table II lists some values for the equilibrium constant for the reaction:

$$H_2O + O \rightleftharpoons 2OH \cdot$$

determined in the several flames indicated. The last column gives values calculated from the JANAF tables.[2] The results are in very good agreement for this equilibrium, which varies only slowly with temperature.

TABLE II

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM CONSTANT
FOR THE REACTION $H_2O + O \rightleftharpoons 2OH$ IN SEVERAL
$H_2-O_2-N_2$ FLAMES AT ONE ATMOSPHERE[a]

Flame Composition (Mole Ratios)			Adiabatic Flame Temp. (°K)	K_{eq}. for $H_2O + O \rightleftharpoons 2OH$	
H_2	O_2	N_2		Exptl.	Calculated
2	1	1	2889	0.50	0.52
2	3		2720	0.33	0.44
2	1	2	2709	0.50	0.43
2	4		2570	C.22	0.37

a/ All cross sections assumed equal at 20 ev.

Table III compares the oxygen dissociation equilibrium for the four flames studied.

It is worth noting from Table III that in flames whose O_2 content varies almost fortyfold, the O atom concentration agrees with theoretical calculations to within a factor of two. The conclusion is that we are quantitatively sampling O and OH simultaneously from H_2-O_2 flames.

TABLE III

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM
CONSTANT FOR THE REACTIONS $1/2\ O_2 \longrightarrow O$[a/]

Flame Composition (Mole Ratios)			Adiabatic Flame Temp. (°K)	Partial Pressures in %			$1/2\ O_2 \longrightarrow O$	
				O		O_2	$K_{eq.}$	$K_{eq.}$
H_2	O_2	N_2		Exptl.	Lit.	Lit.	Exptl.	Lit.
2	1	1	2889	1.6	1.3	2.7	9.8×10^{-2}	7.6×10^{-2}
2	3		2720	3.3	2.8	ca 50.0	4.7×10^{-2}	3.9×10^{-2}
2	1	2	2709	0.77	0.46	1.54	6.2×10^{-2}	3.7×10^{-2}
2	4		2570	2.4	1.6	ca 60.0	3.1×10^{-2}	2.0×10^{-2}

a/ The data are normalized to the calculated O_2 partial pressure assuming
     equal cross sections at 20 ev.

Note: If the ion intensity data are normalized to the theoretical H_2O composi-
         tion data, instead of O_2, then both O and O_2 are about a factor of two
         below theoretical and equilibrium constants are correspondingly
         smaller.

        Some measurements of H atoms were made at 20 ev in four rich-to-
stoichiometric flames. The H^+ results, due to the low sensitivity caused by
the mass separation effect, are less reliable than the O and OH results.
Still, in three out of four of the flames, the equilibrium constant for
$1/2\ H_2 \longrightarrow H$ agreed with literature values to within a factor of two.

        In one very hot flame, we attempted to measure every species of even
minor importance. Table IV shows the raw ion intensities observed at 20 ev,
the values being corrected for mass separation and normalized to make the H_2O
agree with the theoretical vales at the adiabatic flame temperature. With no
attempted correction for relative cross sections or for true temperature of
the burnt gases, the results reflect the expected compositions.

TABLE IV

RELATIVE ION INTENSITIES OBSERVED IN A H_2-O_2-N_2, 2-1-1 FLAME
(T-2889°K) AT 20 EV IONIZING ENERGY[a]

| | Percent | |
	Exptl.	Calc.
H^+	0.75	3.2
H_2^+	2.25	8.8
O^+	0.42	1.3
OH^+	3.2	5.6
H_2O^+	(47.5)	47.5
N_2^+	14.7	29.9
NO^+	0.12	1.0
O_2^+	0.70	2.7

[a] Intensities have been corrected for mass separation by the first power of
the molecular weight and normalized to the calculated H_2O composition.
No corrections for sensitivity have been made.

III. SUMMARY OF EQUILIBRIUM CONSTANTS DETERMINED
SO FAR IN ONE ATMOSPHERE FLAMES

In Table V, we summarize the type of equilibria studied so far and
compare the observed and JANAF calculated values of the appropriate equilibrium
constants. The chlorine dissociation data differ from that reported in the
Tenth Quarterly Technical Summary Report.[3] Since that time, we have repeated
the runs, made corrections to the experimental temperatures, and recomputed the
literature equilibrium constant from JANAF tables. These results support the
idea that quenching of highly reactive species is being accomplished in our
sampling system. It is quite possible that the variations and departures from
literature values are due to essentially analytical difficulties, such as un-
certainties in relative cross sections, fragmentation contributions, depar-
tures from equilibrium in the flame, temperature errors, etc., and are essen-
tially unconnected with quenching ability.

TABLE V

SUMMARY OF EXPERIMENTAL EQUILIBRIUM CONSTANTS
DETERMINED IN ONE ATMOSPHERE FLAMES

Flame				Exptl. Temp. (K°)	K_{eq}			
					Exptl.	Calc.	Exptl.	Calc.
CH_4	CO	O_2	Ar		$CO + 1/2\ O_2 \rightarrow CO_2$		$H_2 + 1/2\ O_2 \rightarrow H_2O$	
1		2	8	2454	36.4	36.0	234	210
1		2.4	8	2457	28.9	36.0	151	210

					$CO + 1/2\ O_2 \rightarrow CO_2$		$0 \rightarrow 1/2\ O_2$	
	1	1		2769	4.9	7.6	24.5	20.4
	4	3		2824	4.5	6.0	22.0	15.9
	2	1		2834	4.8	5.7	22.5	15.1
	3	1		2807	4.4	6.4	20.9	17.0

					$1/2\ Cl_2 \rightarrow Cl$			
	2	1	2.7	2219	1.42	1.58		
	2	1	3.8	2077	1.43	0.85		
	2	1	5.0	1832	0.89	0.37		

H_2	O_2	N_2		Calc. Temp. (°K)	$H_2O + 0 \rightarrow 2OH$		$0 \rightarrow 1/2\ O_2$	
2	1	1		2889	0.50	0.52	10.1	13.2
2	3			2720	0.33	0.44	21.3	25.6
2	1	2		2709	0.50	0.43	16.1	27.0
2	4			2570	0.22	0.37	32.3	50.0

					$1/2\ H_2 \rightarrow H$			
3	1			3004	0.068	0.155		
2	1	1		2889	0.10	0.112		
4	1			2835	0.018	0.100		
5	1			2627	0.025	0.043		

IV. DISCUSSION AND FUTURE PLANS

More detailed study of any of the equilibria mentioned above will probably be done only in conjunction with our studies of unknown or poorly known species. The big remaining question to be quantitatively answered is that of sampling condensible metal-containing species. So far we have only looked at HBO_2 in a H_2-O_2 flame. Work is under way on means of getting metal salts into flames at up to 0.1 per cent by sprays, transpiration, diffusion or a volatile metal compound. Alkemade[4] and co-workers at Utrecht have been unsuccessful in detecting condensible metal-containing species in a sampling system for one atmosphere flames not unlike ours. Both this group and a group under Dr. Gg. Wagner[5] at Göttingen are actively working on the direct sampling of reactive species from flames.

During the next quarter we will continue to study ways of adding metals to the flame and the resulting plugging problems at the first orifice. We plan to try the Studier continuous mode of operation of the Bendix, which has been reported to give a maximum gain in sensitivity of greater than 100. This full gain may not be achieved with the aerodynamic beam and at low electron energies. We will also increase the modulation rate of our beam for better operation and discrimination. Species in the B-O system will be studied as will SH, FeO and alkali metal oxides and hydroxides.

REFERENCES

1. Milne, T. A., and F. T. Greene, "Mass Spectrometric Study of Metal-Containing Flames," Eleventh Quarterly Technical Summary Report, April 1 to June 30, 1964.

2. JANAF Interim Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, December 31, 1960. Revisions through June 30, 1964.

3. Milne, T. A., Tenth Quarterly Technical Summary Report.

4. Alkemade, C. T. J., Verbal communication at Tenth Combustion Symposium. See thesis of A. L. Boers, "Apparatus for Mass Spectrometric Analysis of Flame Gases," University of Utrecht, Holland (1963).

5. H. Gg. Wagner, work to appear in Tenth Combustion Symposium Volume. Also K. H. Homann, M. Moehizuki, and H. Gg. Wagner, Z. F. Physik. Chemie, 37, 299 (1963).

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